PROBABILITY AND STATISTICS IN BOLTZMANN'S EARLY PAPERS ON KINETIC THEORY

Abstract

Boltzmann's equilibrium theory has not received by the scholars the attention it deserves. It was always interpreted as a mere generalization of Maxwell's work or, in the most favorable case, a sketch of some ideas more consistently developed in the 1872 memoir. In this paper, I try to prove that this view is ungenerous. My claim is that in the theory developed during the period 1866-1871 the generalization of Maxwell's distribution was mainly a mean to get a more general scope: a theory of the equilibrium of a system of mechanical points from a general point of view. To face this issue Boltzmann analyzed and discussed probabilistic assumptions so that his equilibrium theory cannot be considered a purely mechanical theory. I claim also that the special perspective adopted by Boltzmann and his view about probabilistic requirements played a role in the transition to the non equilibrium theory of 1872.

1. *OVERVIEW*.

According to a largely diffused view,[1] Boltzmann's work throughout the period 1866-1871 is an attempt to generalize Maxwell's distribution and to formulate it more precisely and completely, both from a formal and from a physical standpoint. However, upon deeper investigation, it turns out that, in this period, Boltzmann worked out an original theory of the state of equilibrium, developing probabilistic concepts which would be fundamental for the transition to the non equilibrium theory. Among these, an outstanding role is played by what I call the concept of *diffuse motion*, which represents the first version of the ergodic hypothesis. Indeed, the analysis of the concept of diffuse motion is one of the theoretical *leitmotivs* of Boltzmann's work during this period and the results obtained by this analysis prepare two essential moves of the non-equilibrium theory of 1872: the collision mechanism and the differential equation of the distribution function (the so-called Boltzmann equation). Let us look more deeply at this point.

It is well known that kinetic (or dynamic) theories of heat in 1850s and 1860s considered a gas as a system of freely moving particles constrained by very general constraints like the conservation of total energy and momentum. Accordingly, many thermodynamical problems could be reduced to the analysis of the mechanical behavior of a system of material points. The research programme pursued by Boltzmann throughout the period 1866-1871 placed itself

[1] See e.g. Brush 1983, Brush 1986; a similar view is claimed also in von Plato 1994, 77, Cercignani 1998, 86, Flamm 1993, 165-166, Bierhalter 1992, 45.

in this general framework, but with some important differences. In the introduction to his 1868 paper, Boltzmann pointed out that the analytical mechanics of his times studied the transformation of a completely specified physical state to another one *via* equations of motion, but in the dynamical theory of heat, this strategy was impossible and useless.[2] Impossible because of the huge number of particles, and useless, as Boltzmann himself often stressed, because the thermodynamic phenomena, and especially the equilibrium state, depend on general parameters only and not on the individual behaviour of the particles. In other words, we surely are not capable to write or to solve the gigantic number of differential equations of motion for the system of points, but this does not mean that the aim of the dynamic theory of heat is hopeless. Actually, we don't need to know each single equation of motion to deduce the long run behavior of the system *as a whole*, because it depends on average quantities (energy, momentum, etc.). Instead of studying single equations of motion, which are able to give us the state of the system in a differential interval of its evolution, Boltzmann used integral principles, like the principle of least action, to get information about an extended portion of the trajectory of a material point: for the real course the action integral is the least in comparison with all the possibile alternative trajectories given the same general constraints. In 1885, J. J. Thomson magisterially expressed the usefulness of this point of view:[3]

> As we do not know much about the structure of the systems, we can only hope to obtain userful results by using methods which do not require an exact knowledge of the mechanism of the system. The method of the Conservation of Energy is such a method, but there are others which hardly require a greater knowledge of the structure of the system and yet are capable of giving us more definite information than that principle when used in the ordinary way. Lagrange's equations and Hamilton's method of Varying Action are methods of this kind.

By using a slogan, we can say that Boltzmann's strategy was to attack the problem in *Hamiltonian style*. By Hamiltonian style I mean here focussing on the fixed elements of the evolution of the system (general constraints, integrals of motion, negligible coordinates) deriving the actual motion as a privileged one among the possibles, rather than following up every differential variation of the huge number of equations given an equally huge number of initial conditions.[4] Boltzmann adopted this general approach for dealing with many thermodynamical issues during his creative period: the mechanical analogy of the second principle in the 1860s, the general theory of equilibrium state in the 1870s, and the problem

[2] Boltzmann 1868a, 49.
[3] Thomson (1885), 307-308.
[4] I'm not claiming that in the history of mechanics there is such a distinct train of thought and eventually that Boltzmann subscribed to it. What I call *Hamiltonian style* is simply a compact way to characterize an understanding of the problem of motion where variational principles and the study of a finite section of the trajectory are considered a valid alternative to the calculation of every force acting on the particles and the analysis of infinitesimal pieces of motion. This approach can be loosely connected with the work of Lagrange, Poisson, Hamilton and Jacobi in analytical mechanics.

of the monocyclic system in the 1880s. In every case, the Hamiltonian style to the mechanical problems was Boltzmann's favourite.[5]

Of course, Boltzmann was not the only one who applied the tecniques of the Hamiltonian mechanics to thermodynamical problems. R. Clausius and C. Szily, for instance, investigated the issue in the same direction. Historically, all these attempts had to face a technical problem: adopting the Hamiltonian style implies to calculate an action integral whose result in general depends on the states at the limits of the integration time. Obviously, these states, which represent the *details of motion*, cannot be known because of the extreme complication of the system of points. Thus, in order to perform the calculation, the details of motion have to be cancelled out. There are many hypotheses which can pursue this goal: Boltzmann used the hypothesis of closed trajectory, R. Clausius and J. J. Thomson supposed a stationary motion, and C. Szily analyzed strictly periodic motions. This problem was common to all the applications of the tools of the analytical mechanics to thermodynamics. But we will also see later on that the perspective on this subject was far from unanimous.

2. *The mechanical analogy of the Second Principle*.

2.1 *Boltzmann's use of the principle of least action*.

Boltzmann's first paper is entitled "Über die mechanische Bedeutung des zweiten Hauptsatzes der Wärmetheorie", and it is dedicated to look for a mechanical analogy of the second principle of thermodynamics. At the beginning of the paper, Boltzmann noted that while the first principle exactly corresponded to the principle of conservation of energy, no similar correspondence existed for the Second Law.[6] This gap had to be filled 'in the spirit of the mechanical theory of heat' finding an analogy in terms of a mechanical principle governing the evolution of a system of freely moving material points. The distinctive character of a gas understood as such a system is the great irregularity of its motion. The molecules are imagined as moving in the most wide variety of directions and velocities at the same time. Historically, this feature has played a crucial role in kinetic theory, but with some remarkable differences. In this section we'll see as the irregularity enters in Boltzmann's derivation of the mechanical analogy of the

[5] It is worth-while to note that Boltzmann initially considered the principle of least action mainly as a useful analytical tool which was particularly 'in fashion' in 1870s German physics (cfr Boltzmann's letter to J. Stefan on June 26th 1870 in Höflechner 1994, II 2-4), but then he gave it an increasingly importance in founding mechanics and the dynamical theory of heat. In his *Lectures on the principles of mechanics*, published in 1904, he defined 'Hamiltonian way of representation' the formulation of the equations of motion by means of the action integral (Boltzmann 1904, II, 214) and considered the action principle and the Hamiltonian approach as the most general foundation of all physics (Boltzmann 1904, II, 135-139).

[6] Boltzmann 1866, 9.

second principle and in the following section we will make a comparison with Clausius' approach.

To begin with, Boltzmann provides a mechanical interpretation of the temperature by means of the concept of thermal equilibrium. His aim is to show that the average kinetic energy has the same general features as the temperature, i.e. at the equilibrium both the temperature and the kinetic energy exchanged are, on average, zero. To accomplish this goal he discusses a model of gas consisting of many particles (molecules), in which he singles out a sub-system of two particles and studies their behavior assuming that they are in equilibrium with the rest of the system. This condition of equilibrium requires that the sub-system and the rest of the particles exchange kinetic energy and changes their state, but in such a way that the average value of the kinetic energy exchanged in a finite interval of time is steadily zero, i.e. the time average of the kinetic energy is stable. However, since the particles exchange energy and momentum with the rest of the system, a mechanical description of this two-particles system is problematic because the usual laws of the elastic collision cannon be applied. Boltzmann circumvented this difficult with a strategy which is, from a modern point of view, odd to say the least. He put forward the following comment which is, at the same time, interesting and misterious:[7]

> After a certain time, whose start and end will be labelled with t_1 e t_2, the sum of the [kinetic energies] of both atoms, as well as the motion of the gravity centres relatively to a certain direction, will again assume the same value.

Schematically, Boltzmann's argument is as follows: since the total energy and momentum of the two-particles system continously change, comparing two different states of the system requires knowing the details of the process, which is pratically impossible. But he supposes that, in the course of the evolution, the system will be found sooner or later in two states with the same total energy and momentum. Of course, the comparison between such states gives the same outcome as if they derived from an elastic collision, so the details of the process do no longer matter.[8] Next, Boltzmann generalizes the result to the other states supposing the equiprobability for the direction of motion and averaging the equation for the elastic collision. Therefore, the entire argument relies on the statement that, at equilibrium, the evolution of the two-particles system is such that, *it sooner or later passes through two states which have the same total energy and the same total momentum*.[9] It is important to point out two surprising elements in this assumption. First, no hint is given about how long the time interval $t_2 - t_1$ has to be: actually only the existence of such an interval does

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[7] Boltzmann 1866, 10.

[8] This point is subtle. In his deep study on the issue, Bierhalter claims that the conservation of the total energy and momentum is Boltzmann's starting assumption (Bierhalter 1992, 34). Actually, it is a consequence of a more fundamental hypothesis.

[9] The conservation of momentum follows from the fact that the direction of motion, i. e. the various components of the velocity, are conserved.

matter. Second, the assumption rests *on the possibility of such states*. Boltzmann gives no explicit arguments to support it, thus the only reasonable foundation he can frame for this astonishing hypothesis is that the occurring of such an event (two states taking place at two different instants with the same total energy and momentum) is not impossible given the general constraints of the evolution of the two-particles system. *Boltmann is simply taking for granted that if these states are able to occur, then they will occur*. Hence, Boltzmann inteprets the irregularity of the system evolution as a sort of spreading out of the evolution among the possibile states. I call this kind of evolution *diffuse*. Thus, in this obscure passage we can found a first embryonic version of the ergodic hypothesis. My claim is that this particular perspective on the irregularity of motion determines Boltzmann's subsequent research on this issue.

Having supposed that two states of the sub-system exist, such that total energy and momentum are constant, Boltzmann goes on with his argument deriving the kinetic energy exchanged by the two particles in passing from a state to another. Of course, he obtains the same result as for an elastic collision:[10]

$$(1) \qquad l = \frac{2mM}{(m+M)^2}\left[MC^2\cos\phi - mc^2\cos\varphi + (m+M)cC\cos\varphi\cos\phi\right].$$

Equation (1) provides the kinetic energy exchanged by the two particles in two particular states. To achieve the average exchanged energy Boltzmann makes the second surprising move of his argument: he considers all the angles appearing in (1) as equiprobable and ascribes this property to 'the molteplicity of the forces acting [on the particles] and to the arbitrariness of the directions of motion of the atoms'[11] following from the irregularity of the motion itself. Thus, introducting an averaging factor in the equation (1), Boltzmann succeeds in obtaining a condition of equilibrium for the average kinetic energy which is analogous to that for the thermal equilibrum. His conclusion is that the temperature is a function of the average kinetic energy of the system.

Boltzmann's next step is the deduction of the mechanical analogy of the Second Law of thermodynamics in the form of the principle of least action. He limits himself to the one-point case and considers an evolution trajectory during the time i such that the material point with mass m moves from configuration s_0 and speed v_0 to configuration s_1 and speed v_1. The application of the principle of least action requires to solve the problem of the details of motion. If E_k is the kinetic energy and U the potential energy, then the principle of least action can be written in the following form:[12]

[10] Boltzmann 1868a, 12.
[11] Boltzmann 1868a, 12.
[12] Cf. Szily, 1872, 342; Bierhalter 1983.

(2) $$\delta A = \delta \int_0^i (E_k - U)dt = \left[\sum mv_1\delta s_1 - \sum mv_0\delta s_0\right] - E\delta i = 0 .$$

Equation (2) consists of two terms: the term in bracket depends on the condition at the beginning and at the end of the trajectory, while the remaining term depends on the general conditions of the motion, i.e. the total energy E and the integration time i. In order to obtain the Second Law of thermodynamics out of equation (2), eliminating the term in bracket, the details of motion, is necessary because we cannot know the exact condition of the system. In a review paper published on the *Philosophical Magazine* in 1872 and entitled "On Hamilton's Principle and the Second Proposition of the Mechanical Theory of Heat", C. Szily summarized the issue discussing three different assumptions able to solve the problem:[13]

(a) All the trajectories start from, and arrive at, the same configurations:

$$\delta s_1 = \delta s_0 .$$

(b) All the trajectories are closed and periodic, i.e. they arrive with the same configurations and motion conditions:

$$\delta s_1 = \delta s_0; \qquad v_1 = v_0 .$$

(c) The law governing the movement of the material points on the trajectory is:

$$v_1\delta s_1 = v_0\delta s_0 .$$

Condition (b), namely the closure of the trajectory, is the condition chosen by Boltzmann. However, he interpreted it in a peculiar way:[14]

> Now we suppose that each atom after a certain time (large as you want) whose start and end we will call t_1 e t_2, comes back to a state of the body with the same speed and direction of motion and in the same place, thus describing a closed course and after that it repeats its motion even if not in the same way, but in a way so similar as the average [kinetic energy] throughout the period $t_2 - t_1$ can be considered the average [kinetic energy] of the atom throughout a period arbitrarily large.

Contrary to Szily, Boltzmann does not require a strict periodicity for the trajectory. Provided the closure of the trajectory, the particle can perform different evolutions as long as the average kinetic energy remains constant.[15] In other

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[13] Szily, 1872, 342.
[14] Boltzmann 1866, 24.
[15] Thus, Martin J. Klein's claim according to which in 1866 Boltzmann supposed a strict periodicity of the trajectory (cf. Klein 1972, 61 and Klein 1973) is not accurate. Jan von Plato's claim (cf. von Plato 1994, 76), according to which Boltzmann's assumption is 'a kind of periodicity assumption' is more accurate

words, Boltzmann is claiming that in the trajectory two instants can always be found in which the particle assumes the same state, *but it is not necessary that the time separating these two instants be always the same*, as in the strictly periodic motions. We do not need a constant period for the motion because, as underlined by Clausius as well,[16] what matter is *if* and not *when* the closure of the trajectory occurs.[17] Boltzmann frames here a concept of motion which is more general than the periodic motion usually adopted in the mechanical analysis of his times and it is clear that this concept is closely connected with the obscure passage above mentioned. Indeed, Boltzmann does not require that the trajectory always crosses the same states, as in the strictly periodic motions, but that it crosses *all the possible states*. If this requirement is fulfilled, we don't need to know the exact form of the trajectory to conclude, as Boltzmann does, that sooner or later the trajectory will be closed.

This assumption, whose first appearance is in the mechanical interpretation of the temperature, is the core of Boltzmann's approach. By using it the argument becomes very sound. He supposes that the variation of the trajectory is due to an infinitesimal quantity of kinetic energy given to the system:

$$\varepsilon = \frac{1}{i}\int_0^i \left(mv\delta v - m\dot{v}\delta r\right)dt\,,$$

where i is the closure time of the trajectory. Hence, the variation of the average kinetic energy is:

$$\delta\left(2i\overline{E}_k\right) = \int_{r_o}^{r_i}\left(m\delta v dr + mvdr\right) = \int_0^i mv\delta v dt + \int_{r_0}^{r_i} mvd\delta r\,.$$

The first integral contains the details of motion and it disappears for the closure of the trajectory. Calculating the remaining integral, interpreting the kinetic energy ε as the quantity of heat δQ, and using the definition of temperature, Boltzmann arrives at:

$$\frac{\delta Q}{T} = \delta\left(\lg(i\overline{E}_k)^2\right),$$

which represent a mechanical formulation of the Second Law of thermodynamics.

To sum up, in this paper, Boltzmann introduces an embryonic version of the ergodic hypothesis in the form of a diffuse motion among the possible states. He implicity, and sometimes explicitly, founds this behavior on the irregularity and complexity of the molecular motion, but, generally speaking, Boltzmann's assumptions and reasonings in this paper are far from transparent: we have seen

[16] Clausius 1871, 173.

[17] Furthermore, the principle of least action requires the conservation of the total energy, but not the syncronization of the trajectories.

that some key passages of his arguments are unclear to say the least. But there is a reason for this obscurity.

Actually, what is striking in Boltzmann's 1866 paper is his creative and flexible use of the mechanical tools and in particular of the principle of least action. His general approach aims for extending the concepts of the analytical mechanics, in particular the variational principles, to the study of mechanical systems with thermodynamical features, and he singles out the diffusion as the distinctive character of such systems. In other words, he does not understand the application of the Hamiltonian style as a mere 'exercise of mechanics', to use a Maxwell's famous phrase, but as a creative process in which a new class of mechanical systems is framed. Of course, this process cannot be free of conceptual tensions, which indeed can be seen in the obscure passages and in the unclear relations among the notions Boltzmann makes use of.[18] But to fully appreciate this point we have to compare Boltzmann's use of the principle of least action with Clausius's.

2.2 *Rudolf Clausius' contribution*.

The study of the connections between thermodynamics and the principle of least action was not Boltzmann's exclusive research programme.[19] At the beginning of 1870s, Rudolf Clausius also treats a similar problem in his papers on the virial theorem and on the mechanical analogy of the Second Law. But Clausius deals with another problem beside the issue of the elimination of the details of motion: the relation between the behavior of a single-point and a multi-points system. This was not a new subject for him. Roughly speaking, the description of a huge number of material points (like a gas, according to the point of view of the kinetic theory) is possible by introducing average values of mechanical quantities (energy, momentum, velocity and so on). However, the same average can be produced by very different populations, hence the extension of mechanical arguments from a single material point to a multi-points system and average values requires some assumptions on the population itself.

A plain example is Clausius' 1859 paper on the mean free path. In this paper Clausius supposes that the average velocity is the product of a population of molecules which 'move at the same rate.'[20] This simplistic assumption allows Clausius to extend the argument for a single molecule to the whole system and, moreover, allows him to consider average values as *representative of the state of the system*: this means that an arbitrary individual state does not significantly

[18] On this issue see section 6.
[19] For an overview see Bierhalter 1987.
[20] Clausius 1859, 84-85.

differs from the average or, in other terms, that the average is more or less stable on the system.[21]

In the 1870s, Clausius proposed a more general point of view on this issue, supposing that the average values derives from a population in which the most different conditions of motion are represented. This again implies, as we will see soon, that the average values truly represent the system and are ‘stable’ during the time. Thus, Clausius related the irregularity of motion expecially to the problem of the transition from a single point to a multi-points system.

Indeed, in his article on the virial theorem,[22] Clausius points out that his interest is directed towards systems ‘in which innumerable atoms move irregularly but in essentially like circumstances, so that all possible phases of motion occur simultaneously.’ He cleverly exploits this assumption for computing the virial of a system of points. The total virial is the sum of the *internal*, due to the potential function $\phi(r)$ acting between molecules at a distance r, and the *external* virial, due to the forces acting on the system in terms of external pressure and change of volume:

$$-\frac{1}{2}\overline{\sum fr} = -\frac{1}{2}\overline{\sum r\phi(r)} - \frac{3}{2}pv\,.$$

The internal virial can be obtained by calculating the summation of $r\phi(r)$ extended over all the possible pair of molecules and averaging the result over the entire trajectory of the system. But, Clausius remarks, if the motion phases are ‘simultaneously’ represented by a large number of particles, the sum of the values of $r\phi(r)$ over each pair of particles, i.e. the virial for an arbitrary istant of the trajectory can replace the time average calculated for each pair of particles because this sum of the values of $r\phi(r)$ ‘does not importantly differ from their total value throughout the course of the individual motion:’[23]

$$-\frac{1}{2}\overline{\sum r\phi(r)} \cong \left(-\frac{1}{2}\sum r\phi(r)\right)_t ,$$

where t is arbitrary. Hence, by using the irregularity of the motion, Clausius obtains a simple expression for the total virial of the system.

Later in the paper, Clausius faces also the problem of the elimination of the details of motion. To prove the virial theorem, Clausius considers a particle whose evolution is described by the standard Newtonian equations:

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[21] We can hardly find this problem in Boltzmann’s 1866 work. At the end of the paper, Boltzmann extends the mechanical analogy to a system of N points, without arising any question about the composition of the population of points (Boltzmann 1868, 27-29). This problem appears more explicitly in his next papers.
[22] A discussion of Clausius’ paper can be found in Bierhalter 1992, 35-36.
[23] Clausius 1870, 125.

$$m\frac{d^2x}{dt^2} = X;\quad m\frac{d^2y}{dt^2} = Y;\quad m\frac{d^2z}{dt^2} = Z,$$

X, Y, Z being the components of the force acting on the system. By simple analytical manipulations, Clausius proves that:

$$\text{(3)}\qquad \frac{m}{2i}\int_0^i \left(\frac{dx^2}{dt}\right)dt = -\frac{1}{2i}\int_0^i Xx + \frac{m}{4i}\frac{d^2(x^2)}{dt^2}\Bigg|_0^i .$$

A feasible integration time i had to be chosen in order to introduce stable averages of the first term on right and on left and to cancel out the last one, i.e. the details of motion. Clausius argued that if the trajectory is closed and periodic and i is chosen equal to the period, then exactly this consequence follows:[24]

> For a periodic motion the duration of a period may be taken as the time *t*; but for irregular motion (and, if we please, also for periodic ones) we have only to consider that the time *t*, in proportion to the times during which the point moves in the same direction in respect to any one of the directions of coordinates, is very great, so that in the course of the time *t* many changes of motion have taken place, and the [average] have become sufficiently constant.

Thus for periodic motion the theorem is easily proved. In order to generalize this result to the case of non-periodic trajectory, Clausius introduced the hypothesis of the *stationary motion*. A motion is said to be stationary if its parameters can assume values strictly included within certain limits. Among the instances of stationary motions, Clausius mentioned periodic mechanical motion, and, of course, atomic and molecular motion.[25] Assuming the stationarity, the details of motion float within given limits, so that they can have only finite values. By choosing the time i large enough, the second term on the right side of the equation (3) becomes smaller and smaller and can be neglected.[26] Clausius applied the same reasoning to the other motion components and, by summing them up, he easily obtained the theorem.

I add some remarks on these results. In order to prove the virial theorem, Clausius analyzes a finite portion of trajectory of a system of material points: the theorem concerns averages, i. e. an interval of time large enough. This fact bring to him the problems of the stability of averages and the elimination of the details of motion. Clausius' strategy to solve these problems has many similarities to Boltzmann's: the irregularity of motion plays a crucial role. However, it is also apparent that Clausius' arguments are mainly limited to well-known examples of mechanic motion: he confines himself to the paradigmatic cases of 'periodic motion – such as those of the planets about the sun – and the vibration of elastic bodies.' Furthermore, the concept of stationary motion slightly differs from a kind

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[24] Clausius 1870, 127.
[25] Clausius 1870, 123.
[26] Clausius 1870, 127.

of constant motion. Probably, in Clausius' intentions, it should be a mechanical correspondent of the quasi-statical process of the thermodynamics. The key features of this concept are the stability of the averages obtained by means of the complexity of the system and the stable oscillation of the mechanical quantities around the mean itself. It is easy to realize that there is scant progress from the simplistic assumption of the 1859 paper. Moreover, the irregularity of motion is understood as an initial condition of the specific problem rather than a fundamental feature affecting the time evolution of the system.

This trend becomes clearer in the paper published the year after and entitled "On the Reduction of the Second Axiom of the Mechanical Theory of Heat to general Mechanical Principles" in which the mechanical analogy of the second principle of thermodynamics is discussed. Clausius' main aim is to find a mechanical correspondence for his thermodynamical equation:

(4) $$dL = \vartheta dZ,$$

where dL is the differential work, ϑ the absolute temperature and Z is Clausius' disgregation function. Provided that the absolute temperature is interpreted as average kinetic energy, to give a mechanical correspondent of the equation (4) means, from Clausius' point of view, figuring out an expression for the variation of work dL and so obtaining a mechanical explanation for the misterious disgregation function dZ. To begin with, he considers a single point performing a closed and strictly periodic trajectory. These assumptions lead to a valuable simplification of his calculations and allow him to arrive at an expression for the variation of the potential energy:

$$\delta U = \delta \overline{E_k} + 2\overline{E_k}\delta \log i.$$

To accomplish his task, Clausius has to obtain an expression linking the variation of the work and the variation of the potential energy. If the variation does not change the form of the potential energy, then δU is simply equal to δL. However, Clausius considers also the possibility that the external disturbance results in an alteration both of the phase trajectory and of the form of the potential function.[27] In particular, he supposes that this transition occurs:

$$\delta U = U + \mu V$$

where V is the new form of the new potential function and μ a constant. At this point, Clausius' argument becomes unclear and full of *ad hoc* assumptions. The first step is calculating the variation of work for a single phase ϕ and a whole period:

$$\delta L_\phi = \delta U_\phi + \mu\left(V_\phi - \overline{V}\right).$$

[27] Some historians (cf. Daub 1969, 322-324) considered Clausius' hypothesis very obscure and unusual. Indeed it leads to an involved and intricate argument.

Here $\overline{V}$ means the average of V over the whole period. By integrating over the phases, the quantity V_ϕ is replaced by the average and Clausius can immediately obtain the previous result. However, generalizing his argument to a multi-points system requires a further appeal to the irregularity of motion:[28]

> We will imagine that, instead of one point in motion, there are several, the motions of which take place in essentially like circumstances, but with different phases. If, now, at any time t the infinitely small alteration of the ergal occurs which is expressed mathematically as U changing into $U + \mu V$, we have for each single point, instead of $\mu(\overline{V} - \overline{V})$, to construct a quantity of the form $\mu(\overline{V} - V)$ in which V represent the value of the second function corresponding to the time t. This quantity is in general not =0, but has a positive or negative value, according to the phase in which the point in question was at the time t. But if we wish to form the mean value of the quantity $\mu(\overline{V} - V)$ for all the points, we have, instead of the individual values which occur of V, to put the mean value $\overline{V}$ and thereby obtain again the expression $\mu(\overline{V} - \overline{V})$, which is =0.

Hence, the irregularity of motion implies that the average value of the function V does not considerably differ from the exact value for an arbitrary phase, so that the two values can be exchanged. Clausius used a similar strategy also dealing with the problem of generalizing the application the principle of least action to a system of points. This requires three assumptions. First, a trajectory has its own potential function even if this function can change in every trajectory. Second, he assumes that the trajectories are closed and periodic and the motion of the system as a whole is a set of periodic motions. Third, Clausius requires every phase of motion being represented by a very large number of atoms:[29]

> Further, we will make a supposition which will facilitate our further considerations, and corresponds to what takes place in the motion which we name heat. If the body the heat-motion of which is in question is chemically simple, all its atoms are equal to one another; but if it is a chemical compound, there are indeed different kinds of atoms, but the number of each kind is very great. Now all these atoms are not necessarily found in likely circumstances. When, for instance, the body consists of parts in different states of aggregation, the atoms belonging to one part move differently from those belonging to the other. Yet we can still assume that each kind of motion is carried out by a very great number of equal atoms essentially under equal forces and in like manner, so that only the synchronous phases of their motions are different. In correspondence with this we will now presume also that, in our system of material points, different kinds of them may occur, but of each kind a very great number are present, and also that the forces and motions are such that at all times a great number of points, under the influence of equal forces, move equally, and only have different phases.

The usefulness of the latter assumption becomes immediately clear. The principle of least action for a single phase is:

[28] Clausius 1871, 170.
[29] Clausius 1871, 174.

(5) $$\int_0^1 \frac{d}{dt}\left(m\frac{dx}{dt}\delta x\right)dt = 0.$$

The elimination of the details of motion follows from the closure and periodicity of the trajectory, but for a system of points a further simplification appears:[30]

As, however, at a fixed time the points belonging to the group have different phases, and the number of the points constituting the group is so great that at every time all the phases may be considered to be proportionately represented, the value of the sum:

$$\sum m\frac{dx}{dt}\delta x,$$

referred to all these points, will not perceptibly vary. The same holds good for every other group of points of like kind and with equal motion; and hence we can at once refer the preceding sum to all the points of our system and likewise regard as constant the sum so completed.

In other words, from the irregularity of the motion the stability of the averages and, as a consequence, the costancy of the summation over the different phases derives. Accordingly, Clausius has not to consider the integral equation (5), but the simpler equivalent:

$$\frac{d}{dt}\sum m\frac{dx}{dt}\delta x = 0.$$

Finally, in order to generalize the theory to the case of non-closed trajectories, Clausius resorted again to the concepts of stationary motion:[31]

Let us first consider only those components of the motions which refer to one determined direction – for example, the components in the *x* direction of our system of coordinates. We have then to do simply with motions alternately to the positive and the negative side; and if, in particular, in relation to elongation, velocity, and duration manifold varieties occur, there yet is in the notion of a stationary motion the prevalence of a certain uniformity, on the whole, in the way that the same states of motion are repeated. Accordingly it must be possible to exhibit a mean value for the intervals of time within which the repetitions take place with each group of points that are alike in their motions.

From these example one can get the clear impression that the irregularity of motion, the stability of the averages, and the hypothesis of stationarity aim for giving 'a certain uniformity' to the evolution of the system. Actually, this is the point of Clausius' approach to the mechanical analysis of a system of point. This

[30] Clausius 1871, 175.
[31] Clausius 1871, 178.

opinion will be shared in 1887 by J. J. Thomson as well. In the second part of a long study dedicated to the application of the mechanical principles to physics Thomson faced the problem of using the principle of least action for the analysis of a system of points:[32]

> If the motion be oscillatory, and *i* a period of complete recurrence; [the term within brackets in (1)] will have the same value [at the beginning and at the end], and therefore the difference of the values will vanish. The case when the motion is oscillatory is not, however, the only, nor indeed the most important, case in which this term may be neglected. Let us suppose that the system consists of a great number of secondary systems, or, as they are generally called, molecules, and that the motion of these molecules is in every variety of phase; then the term [within brackets] taken for all the molecules, will be small, and will not increase indefinitely with the time, but will continually fluctuate within narrow limits. This is evidently true if we confine out attention to those coordinates which fix the configuration of the molecule relatively to its centre of gravity; and, if we remember that the motion of the centre of gravity of the molecules is by collision with other molecules and with the sides of the vessel which contain them continually being reversed, we can see that the above statement remains true even when coordinates fixing the position of the centres of gravity of the molecules are included. Thus if the time over which we integrate is long enough, we may neglect the term [within brackets] in comparison with the other terms which occurs in equation (1), as these terms increase indefinitely with the time.

Notwithstanding the temporal difference, Thomson's analysis fits almost perfectly with Clausius' and it shares the same argument founded on stationary motion.

2.3. *A comparison between Boltzmann's and Clausius' approach*.

We have seen that the application of the principle of least action to the second law of thermodynamics involved a technical problem: the elimination of the details of motion of the action integral. Both Boltzmann and Clausius faces this problem and their solutions are formally similar, but there are also remarkable differences between their approaches. Clausius starts from thermodynamics and his aim is to find a mechanical explication for the disgregation function and the law (4). That this mechanical explication is the principle of least action is scantly commented by Clausius, and the variational nature of this explication does not play any role in his theory. Moreover, Clausius uses the irregular character of motion only to obtain simplification in his calculation about the transition from a single point to a multi-points system, but he never understands the irregularity as a particular feature of the *system evolution as a whole*. Indeed, the problem of the details of motion is solved appealing to paradigmatic kinds of mechanical evolution (closed trajectories, periodic or stationary motion) and to a number of *ad hoc* assumptions.

[32] Thomson 1887, 474.

On the contrary, Boltzmann's approach is mainly characterized by a mechanical standpoint. The fundamental result of his 1866 paper is not that the Second Law has a mechanical analogy, but rather that *this mechanical analogy is just the principle of least action*. Actually, the connection between the irreversibility and the variational principles forms the backbone of his understanding of the thermodynamical phenomena. In other word, Boltzmann's research programme moves from a different question: how can we use the mechanical tools to deal with system which have thermodynamical properties? This question has two consequences for Boltzmann's research programme. First, it requires a flexible perspective on the mechanical concepts and tools so that some new kind of systems and behaviors have to be included within the mechanical framework. Thus, the mechanical analogy of the Second Law represents for Boltzmann an opportunity for a creative use of the mechanical tools which flows into the description of a new type of system: a mechanical system with thermodynamical features. This attempt, of course, induces some internal conceptual tensions in Boltzmann's thought, which we will discuss in the next sections.

Second, Boltzmann is not interested in specific thermodynamical features, but only in the very fundamental ones, like the irreversibility. Contrary to Clausius and to Maxwell, he tries to frame a general theory of equilibrium and non equilibrium, i.e. a broad perspective on these processes rather than one depending on phenomenological aspects like the transport phenomena. This goal can be accomplished only focussing on the general thermodynamical proprieties. In his 1866 paper, Boltzmann moves the first steps in this direction figuring out the concept of diffuse motion and the first primitive version of the ergodic behavior. This step is already outside the boundary of the mechanics of his times. The most part of his equilibrium theory will be dedicated to clarify this concept.

A point is particular meaningful to show how far-reaching is the difference between the two approaches. We see that Clausius rose the problem of the stability of the average values of mechanical quantities (energy, momentum and so on) for a system of points. To solve this problem Clausius introduced the concept of stationary motion, according to which the quantities continuously float around the mean. Indeed, the question itself has a thermodynamical flavor and the solution has a clear correspondence in the quasi-statical process. However, Clausius was only a step away from some important results. In a long review paper written in 1903 as a report of the British Association for the Advancement of Science, G. H. Bryan defines the stationary motion as the hypothesis according to which 'the potential and kinetic energies of the molecules shall fluctuate *rapidly* about their mean value, and there shall be one or more *quasi-periods i* satisfying the definition which will be given in the course of the proof.'[33] Later in his paper, Bryan critizes Clausius' assumption and adds an interesting remark:[34]

> I would therefore suggest that the existence of a quasi-period *i* [...] can be better explained by arguments of a statistical nature based on the immensely large number of the molecules present in a body of finite dimensions. In the steady or stationary motion of such a body, it is reasonable to assume (as in the kinetic theory of gases) that the velocities of the molecules are on the whole equably distributed as regards direction.

Of course, Bryan is speaking after the fact, but the conceptual relation he points out is correct. From the problem of stability to the statistical arguments there is only the idea that the stability results from an equidistribution among many different elementary events. But Clausius missed this opportunity: slightly generalizing his view of 1859, he thought about stability as the result of a fluctuation around the mean. On the contrary, we'll see in the next section how Boltzmann arrived to the equiprobability of the elementary events, and then to the statistical arguments, through the study of the diffuse motion.

3. *EQUILIBRIUM THEORY*.

3.1 *Boltzmann's General Solution to the problem of equilibrium*.

In 1867, James Clerk Maxwell proposed a new and improved version of the theory he had already published in 1860. In his brilliant paper, the Scottish physicist made use of the distribution function giving to it a clear probabilistic meaning. Moreover, he provided a deduction of his famous equilibrium distribution by means of probabilistic considerations. But in Maxwell's paper, the equilibrium distribution played altogheter a secondary role. The main issue he dealt with was to build a feasible picture of the transport phenomena.

The next year, Boltzmann took up the problem with a goal which was entirely new: to create a general theory of the equilibrium state. Boltzmann immediately accepted the probabilistic meaning of the distribution function and the use of statistical arguments, but, from his point of view, Maxwell's treatment of the issue in 1867 was far from being satisfactory, for at least two reasons. First, Maxwell's theory had some gaps due to the lack of mathematical exactness and of physical generality. In particular, it did not account for the effect of potential energy and provided a picture of the collision which was far too superficial.[35]

Second, Maxwell's theory focused on giving an istantaneous ripartition of the kinetic energy, but it did not say anything about the time evolution of a

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[33] Bryan 1903, 88-89.
[34] Bryan 1903, 92.
[35] About this point cf. Boltzmann 1872, 319, note 1.

system. The equilibrium state was understood as characterized by a particular distribution, but the problem of expressing a general condition for a finite trajectory of a system in equilibrium was completely neglected. To pursue his project, Boltzmann needed an expression for the distinctive general feature of the equilibrium state, i.e. his stability in time evolution. Thus, Boltzmann felt that there was a lot to say about the free evolution of a system of points in Hamiltonian style, but, in order to accomplish that, a translation of the equilibrium condition expressed by Maxwell's distribution for a specific state in an analogous condition holding for the whole evolution of the system was required.[36]

All these elements have to be taken into consideration in evaluating the paper in which Boltzmann worked out his equilibrium theory. In fact, the generalization of Maxwell's distribution which can be found in it does not represent the essential aim of the article, but rather simply a step in the direction of a more general equilibrium condition for the whole trajectory.[37] Even more importantly, the particular theoretical background with which Boltzmann faced the problem of equilibrium pointed him toward the non equilibrium problem. Contrary to Maxwell and Clausius, Boltzmann's focus was not on a particular state but on the entire evolution, and this perspective, which is far more abstract and less phenomenological than Maxwell's and Clausius', helped the transition to the non equilibrium theory. Clausius' thermodynamics was essentially limited to the equilibrium state and to processes which differ infinitesimally from it. A similar view was shared by Maxwell whose investigation in the non equilibrium case were strictly confined within the ambit of the transport phenomena. On the contrary, Boltzmann was the only one to overcome this phenomenological point of view and to build a general theory of the non equilibrium state. The historical and conceptual reasons of this move can be found in the standpoint from which he faced the equilibrium theory. I will return on this point in section 4.

Boltzmann's paper is divided into two parts. In the first five sections, he investigated Maxwell's distribution and applied it to more and more complex cases treating external forces, potential energy, motion on one, two and three dimensions and so on. Next, Boltzmann introduced for the first time the combinatorial argument. He explicited the condition of fixed total energy: this implies that one generalized coordinate is determined by the remaining, namely, in modern terminology, a hypersurface of constant energy is defined. Within this hypersurface, the remaining generalized coordinates are still mutually independent and hence Boltzmann was able to develop a combinatorial theory anticipating his famous 1877 memoir.[38] The combinatorial argument put forward

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[36] The claim according to which Boltzmann focused on Maxwell's work after 1866 is maintained by Klein as well (cf. Klein 1972, 62). However, no hypothesis concerning the relationship between Boltzmann's interest for the theory of equilibrium and the previous work on the second principle is framed.

[37] Accordingly, the historical reconstructions deeming the 1868 paper only a kind of Maxwell's 'exercise of mechanics' (cf. Klein 1973, Brush 1983, 62) should be considered inaccurate.

[38] Boltzmann 1868a, 84-84; Boltzmann 1877, 175-186.

in 1868 represents an original way of attacking the problem of equilibrium and something completely different from the contemporaty attempts in the same field. No wonder that it was for the most part misunderstood.

The last part of the article contains the *allgemeine Lösung* (General Solution) to the problem of equilibrium, which is the real core of Boltzmann's conception.[39] His argument is not completely clear and indeed it will be improved in 1871, but the fundamental idea is transparent. He discusses a system of points with mass m_i ($i = 1, \ldots, n$) finding themselves within the volumes $ds_i = dx_i dy_i dz_i$ of the configuration space and $d\sigma_i = du_i dv_i dw_i$ of the velocity space. The total energy of the system is fixed, thus one velocity coordinate is automatically determined and the distribution function can be written as $f(ds_1, \ldots, ds_n, d\sigma_1, \ldots, d\sigma_{n-1}, d\omega)$ where $d\omega$ is an elementary phase surface defined by:

$$d\omega = \frac{c_n}{w_n} du_n dv_n ,$$

where c_n is an unimportant constant. After a time interval δt, the coordinates will be ($i = 1, \ldots, n$):

$$\left.\begin{aligned} x_i' &= x_i + \delta x_i \\ y_i' &= y_i + \delta y_i \\ z_i' &= z_i + \delta z_i \end{aligned}\right\} \Rightarrow ds_i' = ds_i + \delta ds_i$$

$$\left.\begin{aligned} u_i' &= u_i + \delta u_i \\ v_i' &= v_i + \delta v_i \\ w_i' &= w_i + \delta w_i \end{aligned}\right\} \Rightarrow d\sigma_i' = d\sigma_i + \delta d\sigma_i$$

Introducing the potential function $\chi(ds_1, \ldots, ds_n)$ which depends on the system configuration, Boltzmann writes two sets of equations describing the behaviour of the system during the time interval δt:

$$\begin{cases} \delta x_i = u_i \delta t \\ \delta y_i = v_i \delta t \\ \delta z_i = w_i \delta t \end{cases}$$

$$\begin{cases} m_i \delta u_i = \dfrac{d\chi}{dx_i} \delta t \\ m_i \delta v_i = \dfrac{d\chi}{dy_i} \delta t \\ m_i \delta w_i = \dfrac{d\chi}{dz_i} \delta t \end{cases}$$

Now, the independence of the phase variables implies ($i = 1, \ldots, n$):

[39] Boltzmann 1868a, 92-96.

(6)
$$\frac{d\delta x_i}{dx_i} = \frac{d\delta y_i}{dy_i} = \frac{d\delta z_{i-1}}{dz_{i-1}} = 0$$
$$\frac{d\delta u_i}{du_i} = \frac{d\delta v_i}{dv_i} = \frac{d\delta w_{i-1}}{dw_{i-1}} = 0$$

(7)
$$\frac{d\delta z_n}{dz_n} = \frac{dw_n}{dz_n}\delta t = \frac{\delta w_n}{w_n}.$$

Putting together the equations (6) and (7), Boltzmann obtains a general relation expressing the transformation law of the phase volumes:

(8)
$$ds_1' ... d\sigma_{n-1}' d\omega_n' = \left(1 + \frac{\delta w_n}{w_n}\right) ds_1 ... d\sigma_{n-1} d\omega_n .$$

The equation (8) shows, though not yet in a completely straightforward way, that the phase volume is invariant relatively to the particles' motion, that is, the evolution of the system takes place passing through regions of equal phase volume. In this paper, like in all his works on kinetic theory, Boltzmann adopts a relative-frequency definition of probability: the probability attributed to a certain phase region is the ratio of the sojourn time spent by the system in that region to the total time. According to this interpretation, Boltzmann immediately gives a probabilistic meaning to the equation (8) understanding it in terms of equal sojourn time, namely equiprobability, of elementary regions. Furthermore, the density f for the individual configuration[40] turns out to be constant on the whole phase space:

(9)
$$\frac{c_n}{w_n} f(x_1,...,v_n) ds_1 ... d\sigma_{n-1} d\omega_n = \frac{c_n'}{w_n'} f(x_1',...,v_n') ds_1' ... d\sigma_{n-1}' d\omega_n' ,$$

the equation (9) holding for every couple of transformations. From that Boltzmann derives two important consequences.[41] First, the probability attributed to an individual phase region is proportional to the volume of the region itself. Second, considering k successive transformations, it turns out:

(10)
$$c_n f(x_1,...,v_n) = c_n^{(k)} f(x_1^{(k)},...,v_n^{(k)}) ,$$

The equation (10), which is the most important result of the 1868 article, suggests many interesting remarks.

First, it is just the result Boltzmann was looking for: it expresses a condition of equilibrium for the time evolution of the system. The equations (8), (9) e (10) claim the invariance of the elementary volume, the dependency of the

[40] Note that the density f is a density of the individual states of the system. In a modern terminology it can be called a density on the μ-space.

[41] Boltzmann 1868a, 95.

probability on the size of the region and the constancy of the equilibrium distribution function. These results hold for the whole trajectory. Furthermore, note that the equation (8) is a special case of the well-known Liouville theorem. However, Boltzmann never explicitly states this similarity.

Second, Boltzmann gives to the concept of diffuse motion obscurely framed in 1866 a clearer formal expression making a very surprising move: he generalizes the equations (8), (9) and (10) *to the whole available phase space, i.e. the whole hypersurface defined by the conservation of total energy*. This amounts to say (a) that the system passes through all the elementary regions; (b) that the initial and final states of a trajectory are irrelevant, since all the elementary regions are equivalent *regarding to the phase volume*; (c) that the result of the mechanical analysis depends on general constraints only, in this case on the total energy. It is apparent that the point (a) specifies a formal expression for the diffusion, and the points (b) and (c) justify the analysis of finite trajectory of motion. Hence, the concept Boltzmann had implicitly supposed in 1866 has now the form of a completely new mechanical tool: *the Liouville theorem generalized to the whole allowed space*. I call this particular generalization the Boltzmann-Liouville theorem.

Third, the equiprobability of the elementary regions implies that Maxwell's distribution derives from a uniform probability density on those elementary regions, and this justifies Boltzmann's combinatorial analysis. Let us look more deeply at this point. In the 1868 paper, Boltzmann derives the equilibrium distribution by means of an original combinatorial argument. A similar strategy is put forward also in his great 1877 memoir. Even though the arguments have a different structure,[42] both rely on the same fundamental idea: differently combining a set of equally possible elementary events. Of course, the question arises on which events can be considered *elementary*. The Boltzmann-Liouville theorem gives an immediate answer to this question: each infinitesimal region in the $(2n-1)$-dimensional phase space of the system is elementary in a mechanical sense, because (1) these regions have the same volume and (2) the trajectory crosses, sooner or later, each region. Provided that the probability associated with a region is its phase volume,[43] Boltzmann gets a straightforward relation between the probability concept and the mechanical evolution of the system. This is the fundamental step in Boltzmann's mechanical understanding of the probabilistic arguments.

Fourth, interpreting the phase space density as probability attributed to a region, Boltzmann introduced a primitive version of the concept of state

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[42] In particular, the 1868 argument rests on a *marginalization* of the distribution function, while the 1877 argument exploits a *maximization* of it.

[43] This assumption is nowadays known as absolute continuity of probability measure and phase measure.

probability. Martin J. Klein[44] claimed that Boltzmann did apply the probability to the system as a whole only in 1877 and that, previously, the concept of probability concerned single particles only. In fact, in 1868 Boltzmann understood the distribution function in probabilistic terms and regarded this function as a feature of the system as a whole, and this interpretation was maintained by Boltzmann again in the 1871 version of the equilibrium theory.[45]

3.2 *Maxwell's objection*.

We have seen that the Boltzmann-Liouville theorem (i.e. the Liouville theorem generalized to the whole allowed phase space) is the crucial move in the 1868 paper. However, a problem arises: what exactly is the status of this result? Indeed, although the Liouville theorem seems a straightforward consequence of the dynamic character of the particles' motion, its generalization to the whole phase space is not justifiable from a dynamical point of view. Maxwell was well aware of this point and actually in 1879, in a paper written few weeks before his death, he sharply criticized Boltzmann's argument pointing out its presuppositions and reframing it in a personal way.[46] The most remarkable aspect of Maxwell's paper is the formal clearness with which the conclusion follows.[47]

Assuming the total energy conservation and Hamilton equations among the generalized co-ordinates $q_1, \ldots, q_n$ and momenta $p_1, \ldots, p_n$ and using the concept of action, Maxwell gets the following relation between the initial volume $dsd\sigma$ and the final one $ds'd\sigma'$:

(11) $$ds'd\sigma' = dsd\sigma \, .$$

The equation (11) precisely expressed the theorem derived by Boltzmann, i.e. the invariance of the elementary phase volume. As the total energy E is fixed, one phase coordinate, e.g. the momentum p'_1, can be eliminated; some substitutions yield:

(12) $$dq'_1 \ldots dq'_n dp'_2 \ldots dp'_n \frac{1}{\dot{q}'_1} = dq_1 \ldots dq_n dp_2 \ldots dp_n \frac{1}{\dot{q}_1} .$$

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[44] Cf. Klein 1973, 83-84.
[45] Cf. Boltzmann 1871b, 239-240.
[46] Note, incidentally, that the problem of the invariance of the elementary phase regions can be found in Maxwell's papers as well. Since Maxwell's deduction of the form of the distribution function requires a close comparison between the distribution functions before and after the collision, it relies on the invariance of the elementary volumes (Maxwell 1867, 44-45). This aspect could not escape a mind as interested in analytical issues as Boltzmann's. Not by chance, in 1872, Boltzmann will mention the invariance of the elementary volumes as a result whose proof 'was provided by Maxwell and then significantly generalized by me' (Boltzmann 1872, 333).
[47] Moreover, in 1871, Boltzmann himself had made a number of attempts to give his argument much clarity keeping the same structure. In any case, it is very probable that Maxwell did not know these Boltzmann's papers.

Maxwell points out that, strictly speaking, the equation (12) holds only for the phases actually passed through by the system throughout its dynamic evolution. In other words, in order to know which regions have the property (12), it would be necessary to know the corresponding details of motion: 'the motion of a system not acted on by external forces satisfies six equations besides the equation of energy, so that the system cannot pass through those phases, which, though they satisfy the equation of energy, do not also satisfy these six equations.'[48] However, Boltzmann had supposed the equation (12) to be constrained by the conservation of energy only, so that the equiprobability of the elementary phase regions immediately followed. As Maxwell notes, such a move surreptitiously needed the ergodic hypothesis: 'the only assumption which is necessary for the direct proof [of the theorem] is that the system, if left to itself in its actual state of motion, will, sooner or later, pass through every phase which is consistent with the equation of energy.'[49]

To justify this hidden assumption in Boltzmann's theorem, Maxwell suggests a physical mechanism based on the collisions against the walls of the vessel. Thus, Maxwell claims that Boltzmann's move is not justifiable by means of the mere internal dynamics of the system, but, for its explanation, it requirs some kind of external influences, whose features remain unknown. In other words, Maxwell's analysis makes clear the ambiguous nature of the hypothesis of diffuse motion: he shows that it is constituted of both dynamic and probabilistic elements, and the latter follows from our ignorance of the external influences on the system.

Moreover, Maxwell's analysis does not miss another consequence of the equation (12) either: since the distribution function is a function of the phase coordinates only, it follows that it is constant on the whole phase space. Accordingly, the probability attributed to each phase regions also depends only on the volume of the region itself. These consequences are connected to the ergodic hypothesis as well:[50]

> If the distribution of the N systems in the different phases is such that the number in a given phase does not vary with the time, the distribution is said to be steady. The condition of this is that [the distribution function] must be a constant for all phases belonging to the same path. It will require further investigation to determine whether or not this path necessarily includes all phases consistent with the equation of energy. If, however, we assume that the original distribution of the system according to the different phases is such that [the distribution function] is constant for all phases consistent with the equation of energy, and zero for all phases which that equation shows to be impossible, then the law of distribution will not change with the time and [the function] will be an absolute constant.

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[48] Maxwell 1879, 714.
[49] Maxwell 1879, 714.
[50] Maxwell 1879, 722.

Therefore Maxwell was aware that the invariance of the phase volume generalized to the whole phase space is not a purely dynamic assumption.[51] The different perspective from which Maxwell and Boltzmann understood the role of this assumption depends on their respective theoretical course. Boltzmann came from the mechanical study of the evolution of a system of material points where diffusion played an essential role by providing the elimination of the details of motion and, eventually, the stability of the averages. The transition to the statistical analysis essentially meant for Boltzmann a clarification of the concept of diffusion. On the contrary, Maxwell came from the thermodynamical study of the equilibrium state where diffusion played no role as we have seen discussing Clausius' approach. Thus, it is no wonder that he mainly considered the diffusion hypothesis as a hidden assumption in Boltzmann's argument.

3.3 *The definitive form of the equilibrium theory: 1871 trilogy.*

In 1870 and 1871, Boltzmann spent time doing research in Heidelberg and Berlin, working with Kirchhoff and Helmholtz on the problems of electrodynamics.[52] But during that period, he was independently dealing with the issues of kinetic theory. The result of this scientific activity was a series of three papers published in 1871, where his work found a new synthesis. These papers summed up his research about the equilibrium problem and prepared the transition to the non equilibrium theory. The aim of these articles is threefold: to provide a more accurate proof of the Boltzmann-Liouville theorem, to clarify the concept of diffusion, and to give it a mechanical foundation.

Already in the first paper of the trilogy, where the problem of the equilibrium is taken up again, Boltzmann makes clear the crucial role played by diffusion and its connection with probability: 'the different molecules of the gas will pass through […] all the possible states of motion and it is clear that it is of the highest importance to know the probability of the different states of motion.'[53] Boltzmann suggested two kinds of mechanical foundation for diffuse motion.[54]

The first foundation is given by internal collisions and by the external forces acting irregularly on the system of points:[55]

> The great irregularity of the thermal motion and the multiplicity of the forces acting on the body from outwards make probable that its atoms […] pass through all the possible positions and speeds consistent with the equation of energy.

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[51] About these issues see also von Plato 1991; 1994, 94-102.
[52] Many information on this period of Boltzmann's scientific life can be found in Höltz and Laaβ 1989 and in Höflechner 1994, 20-24.
[53] Boltzmann 1871b, 237.
[54] See also von Plato 1991, 77.
[55] Boltzmann 1871c, 284.

Therefore, like Maxwell will do in 1879, Boltzmann claims that the external influence can be a reason of irregular behaviour at a microscopic level.

The second foundation concerns the intrinsic features of the particles' motion and the role of the collisions. Indeed, as early as 1871 Boltzmann begins to deem the molecular collisions as a dispensable requirement. In fact, already in this first paper Boltzmann proposes a new argument for proving the Boltzmann-Liouville theorem, from which a new view of the diffuse motion emerges.[56] He considers a system whose material points are governed by the following equations of motion:

(13)
$$\frac{d\xi_1}{dt} = \chi_1, \frac{d\eta_1}{dt} = \chi_2, \frac{d\zeta_1}{dt} = \chi_3, \ldots, \frac{d\zeta_{r-1}}{dt} = \chi_{3r-3}$$
$$\frac{du_1}{dt} = \lambda_1, \frac{dv_1}{dt} = \lambda_2, \frac{dw_1}{dt} = \lambda_3 \ldots, \frac{dw_r}{dt} = \lambda_{3r}$$

where the χs are function of the velocity components and the λs, are function of the point positions. The equations (13) determines the state of the system at $t' = t + \delta t$ when such a state is known at t. Furthermore, Boltzmann frames the hypothesis that positions and velocities of the initial state are mutually independent, while, evidently, those of the successive state are function of the initial ones. From the differential calculus it turns out:

$$ds'd\sigma' = \left| \frac{\partial(\xi_1', \ldots, w_r')}{\partial(\xi_1, \ldots, w_r)} \right| ds d\sigma .$$

Choosing a time interval small enough, the evolution of the system can be considered as an infinitesimal variation:

$$\xi_1' = \xi_1 + \delta\xi_1, \ldots, w_r' = w_r + \delta w_r ,$$

from which, by means of differentiations, the following set of equations can be obtained:

$$\frac{\partial \xi_1'}{\partial \xi_1} = 1 + \frac{\partial \delta \xi_1}{\partial \xi_1}; \quad \frac{\partial \xi_1'}{\partial \eta_1} = \frac{\partial \delta \xi_1}{\partial \eta_1}; \quad \ldots \quad \frac{\partial \xi_1'}{\partial w_r} = \frac{\partial \delta \xi_1}{\partial w_r}$$
$$\frac{\partial \eta_1'}{\partial \xi_1} = \frac{\partial \delta \eta_1}{\partial \xi_1}; \quad \frac{\partial \eta_1'}{\partial \eta_1} = 1 + \frac{\partial \delta \eta_1}{\partial \eta_1}; \quad \ldots \quad \frac{\partial \eta_1'}{\partial w_r} = \frac{\partial \delta \eta_1}{\partial w_r}$$
$$\ldots$$
$$\frac{\partial w_r'}{\partial \xi_1} = \frac{\partial \delta w_r}{\partial \xi_1}; \quad \frac{\partial w_r'}{\partial \eta_1} = \frac{\partial \delta w_r}{\partial \eta_1}; \quad \ldots \quad \frac{\partial w_r'}{\partial w_r} = 1 + \frac{\partial \delta w_r'}{\partial w_r}$$

These equations can be arranged in a Jacobian matrix so that, neglecting the infinitesimals of higher order, the functional determinant becomes:

[56] Cf. Boltzmann 1871b, 241-245.

(12) $$\left|\frac{\partial(\xi_1',\ldots,w_r')}{\partial(\xi_1,\ldots,w_r)}\right| = 1 + \frac{\partial\delta\xi_1}{\partial\xi_1} + \ldots + \frac{\partial\delta w_r}{\partial w_r}.$$

From the equation of motion, Boltzmann derives the following systems of equations for positions and velocities:

$$\begin{cases}\delta\xi_1 = \chi_1\delta t \\ \ldots \\ \delta\xi_{r-1} = \chi_{r-1}\delta t\end{cases} \qquad \begin{cases}\delta u_1 = \lambda_1\delta t \\ \ldots \\ \delta w_r = \lambda_r\delta t\end{cases}$$

Substituting in the equation (12), considering the infinitesimal time interval constant, and remembering that the χs and the λs do not contain the coordinates relative to which the derivation is performed, it can be obtained:

$$\frac{\partial\delta\xi_1}{\partial\xi_1} = \ldots = \frac{\partial\delta w_r}{\partial w_r} = 0,$$

$$\left|\frac{\partial(\xi_1',\ldots,w_r')}{\partial(\xi_1,\ldots,w_r)}\right| = 1,$$

from which $dsd\sigma = ds'd\sigma'$ and, as a consequence, the invariance of the density, $f(s, \sigma) = f_1(s', \sigma')$ follow. Boltzmann generalizes again this result to all the values, consistent with the principle of conservation of energy, i.e. to ‘all the possible values.’[57]

Boltzmann was perfectly aware of what Maxwell would claim eight years later, namely that the proved invariance holds only for the trajectory that effectively takes place. Indeed, he wrote that the distribution function can be obtained at $t + \delta t$ *only if it is given at t*. However, if the coordinates can assume all the possible values, then there is only one trajectory in the phase space, thus the distribution function is independent of the details of motion and can be immediately computed.

Boltzmann did not miss another important consequence of this perspective: the equilibrium distribution can be obtained without using the collision analysis. An explicit attempt in this direction was pursued by him in a paper entitled “Einige allgemeine Sätze über Wärmegleichgewicht,” where the influence of what I have called Hamiltonian style is very evident. Boltzmann’s main aim is to develop an analogy between his 1868 theorem and Jacobi’s principle of the last multiplier. Boltzmann supposes that $2n - k$ among $\varphi_1, \ldots, \varphi_{2n}$ integrals of motion are fixed, i.e. known, while the remaining k can assume any value within the new phase hypersurface. Accordingly, from the diffusion hypothesis on the new surface, an expression for the distribution function follows:

[57] Cf. Boltzmann 1871b, 243-244.

(15) $$f(q_1,...,p_k)dq_1...dp_k = \frac{Cdq_1...dp_k}{\left|\frac{\partial(\varphi_{2n},...,\varphi_{k+1})}{\partial(q_n,...,p_{k+1})}\right|},$$

with C constant.

Boltzmann writes about equation (15):[58]

> We can immediately derive [the distribution function] as soon as we know the integrals [φ_{2n}, …, φ_{2n-k}] being unnecessary to know anything else about the kind of variation of [q_1, …, p_k].

In other words, as long as the diffuse character of the motion holds, it is unnecessary to take into account collisions or the general evolution of the phase coordinates.[59]

These remarks show that in 1871 Boltzmann began to understand the role of the molecular collisions under a new perspective: from an active mechanism of thermodynamics processes, the molecular collisions became simply a background assumption whose task was to guarantee the diffusion. Moreover, Boltzmann explored the possibility of introducing a foundation for diffusion different from internal collisions and external forces, and of considering the diffuse motion as a fundamental consequence of a complex system. In "Einige allgemeine Sätze" Boltzmann proposes a model of mechanical motion in which the diffuse feature does not depend on internal collisions. He discusses a trajectory in a limited hypersurface[60] and notes that knowing one coordinate allows us to establish the others. But different kinds of motion can be given where that does not happen. He imagines a point moving around a centre of force attracting it with a force $(a/r) + (b/r^2)$. The resulting motion is constituted by a series of ellipses. If the angle formed by the apsidal lines of two consecutive ellipses is an irrational multiple of π, a precession of the elliptical orbit takes place and the resulting trajectory will tend to fill all the circular region between the circumferences described by the major apsis and the one described by the minor apsis. This motion finds an analogy in the well-known Lissajous figures and it fills the whole available phase space.[61] Boltzmann's comment stresses two interesting consequences.

The first consequence is that for such a motion the concept of probability as sojourn time in a phase region can be defined, since only if *all* the phase regions can be crossed by the system, the concept of probability as a longer or shorter sojourn in a certain region is completely defined.[62] The second consequence is that for a diffuse motion the phase coordinates 'are mutually

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[58] Boltzmann 1871c, 277.
[59] Note that, in a broader sense, the equation (13) is clearly analogous to Gibbs' microcanonical distribution.
[60] Boltzmann 1871c, 269.
[61] See von Plato 1994, 94.
[62] Boltzmann 1871c, 270.

independent (only they limit each other within given limits).'[63] By knowing one phase coordinate, we are not able to establish the others, but we can only define a new hypersurface, whose dimension is less than the original one, where we can find it. Thus Boltzmann, even if vaguely and incompletely, links the concept of diffuse motion to two concepts that can be found in the modern ergodic theory: the probability definition and the independence of the phase coordinates. In his next papers, Boltzmann's attitude towards the collisions will be ambivalent: he does not abbandon them completely, but he feels that their role has to be reappraised.

The last paper of the 1871 trilogy, "Analytischer Beweis des zweiten Hauptsatzes der mechanischen Wärmetheorie aus den Sätzen über das Gleichgewicht der lebendigen Kraft", has attracted historian's attention more than the others because it expressly deals with the Second Law and it represents a natural link of conjuction with the non equilibrium theory. In this paper, Boltzmann faces once again the problem of 1866: searching for a mechanical analogy of the Second Law. The article was written as a consequence of a controversy with Clausius about priority[64] and shows the great advancements made by Boltzmann not only in comparison with the beginning of his research programme, but also in comparison with other physicists. The condition of closure for the phase trajectory is abandoned and replaced by a probabilistic analysis:[65]

> If the orbits of the atoms are not closed and the probability of the different position of the atoms is undetermined, special cases can be found where $\delta Q/T$ is not an exact differential. Thus, the transposition of the prove for this case is possible, in the exactest way, only considering such a probability.

Furthermore, also the issue of the stability of the averages with exact values makes its appearance:[66]

> If the body is constituted by a very large number of atoms having together the same states as a single atom passes through during a large time, then every time that an atom gets a certain kinetic energy, an other one loses it and the quantity of E, at a certain time, does not differ from the average of E calculated on a very large interval of time.

In modern terms, Boltzmann's statement is tantamount to saying that the phase average of a quantity defining the physical state is equal to its (infinite) temporal average. But the advantages of the statistical analysis becomes even more apparent when Boltzmann, implicitly continuing the controversy, shows that the main problem of Clausius' article, the variation of the potential function, can

[63] Boltzmann 1871c, 270.
[64] Cf. Boltzmann 1871a, Clausius 1872, Daub 1962. Boltzmann considered very important his priority in the discovery of this particular application of the principle of least action. See e.g. the letter to Leo Königsberger in 1896 (Höflechner 1994, II 267-268).
[65] Boltzmann 1871d, 295.
[66] Boltzmann 1871d, 297.

be dealt with in a simpler and more effective way. The diffusion of motion permitts the replacement of the exact value of the potential χ with its average and the computation of this average requires, of course, the distribution function f. Accordingly, the variation can be written:

$$\delta\overline{\chi} = \delta \int \chi f ds = \int \chi \delta f ds + \int \delta \chi f ds,$$

where the integral holds for the whole trajectory length s.

In other words, in the variation of the potential energy there are two terms to take into account. The first is due to the variation of the position of atoms, i.e. to the change of the distribution function f, the second is due to the variation of the form of the potential function χ. The latter was the case discussed by Clausius, but Boltzmann immediately dismisses it claiming that the change of the forces not involved in performing work (remember that the position of the atoms remains unchanged) makes this term irrelevant in order to evaluate the variation of the potential energy. Clausius' obscure reasoning is simply overcome by an argument based on the distribution function. Furthermore, Boltzmann obtains the following equation:

$$-\overline{X\delta x + Y\delta y + Z\delta z} = \int \chi \delta f ds.$$

There is no hint of the fact that this formula represents a definition of Clausius' virial, but the connection is clear: using the distribution function, Boltzmann obtains all the results previously derived by Clausius, presenting them with a far clearer and terser argument. From this point of view, the article can be considered a contribution to the controversy about the mechanical analogy of the second principle.

Thus, in the 1871 trilogy, the concept of diffusion is clarified by means of many concepts which can be found in the modern view of ergodicity (independence of phase coordinates, link with the definition of probability function, equivalence between the instantaneous behaviour of a system and the behaviour of its constituents during a long time), even if their formulation is not yet completely clear and their mutual relationships are still at a superficial level.

4. *THE CONCEPT OF PROBABILITY*.

In Boltzmann's theory of equilibrium, wide use is made of probability, probabilistic assumptions and statistical arguments; however, this use is not free from ambiguities. We can distinguish three concepts of probability which a physical meaning can be related to; some of them are explicitly developed, some others are merely suggested or implicit. Occasionally the term "probability" is applied also in the epistemic sense of degree of belief.

In most cases, Boltzmann's concept of probability has two characteristics: (1) it is interpreted as sojourn time and (2) it is of use for the calculus of averages.[67] In other words, it is a *relative-frequency concept* and *not an autonomous one*: probability is not a primitive concept, but it has to be related to a mechanical foundation and it is understood as a tool for the calculation of averages.

The relative-frequency meaning appears in Boltzmann's first article and always has a privileged role.[68] Jan von Plato suggested that the relative-frequency definition of probability was adopted by Boltzmann in relation to the interpretation of thermodynamic parameters as average mechanical quantities.[69] Actually, if the temperature is understood as temporal average of the kinetic energy, then the probability of a certain velocity becomes the temporal average of all the possible velocities. Note that, in this sense, Boltzmann's definition is strictly empirical: the value of probability does not follow from the general conditions in which the system is found, but from the real development of a physical process. Thus, the definition of probability as sojourn time requires, in principle, a physical measurement process over a sufficiently long period. Boltzmann, anyway, never specified how long that period had to be.

Furthermore, in some places, a second concept of probability can be found which is quite near to the classical view. In "Lösung eines mechanischen Problems," a brief paper published in 1868 in which the Boltzmann-Liouville theorem is deeply investigated, Boltzmann defined the probability of a certain trajectory constrained by values of some general parameters as the ratio between the number of trajectories having those constraints and the number of all possible trajectories.[70] In 1871 an analogous definition appeared as well, and Boltzmann tried to unify the classical definition and the concept of sojourn time.[71] Moreover, the classical concept of probability as ratio between favorable and possible cases is widely used in Boltzmann's combinatorial arguments of 1868 and 1877.

Moreover, the classical meaning also appeared in the problematic concept of equiprobability. Assumptions can often be found in Boltzmann's papers concerning the equiprobabilities of directions of motion, positions and so on. Even though this concept could be translated in relative-frequency terms, it is not justifiable in an empirical way. Rather, the justification of equiprobability is connected with the indifference principle applied to the parameters (directions, coordinates) within a space of possible values. Accordingly, the equal probability does not derive from a measurement, but from the definition of general conditions and from the indifference principle.

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[67] Cf. e.g. Boltzmann 1871b, 237
[68] Cf. Boltzmann 1866, 13; 1868, 50-51, 66, 70; 1871c, 270; 1871d, 288, 293.
[69] Cf. (von Plato 1991; 1994, 76-77).
[70] Boltzmann 1868b, 98.
[71] Cf. Boltzmann 1871c, 277-278.

Note that the concept of equiprobability does not concern the evaluation of averages, but it represents the prototype of the state probability which will be developed in 1877. The concept of state probability is characterized by autonomy (i.e. it is not adopted only to perform averages calculations) and by the fact that it is applied to the system as a whole, two properties shared with the concept of equiprobability. Moreover, the probabilistic meaning of the distribution function is a further step toward the concept of state probability. Thus, Martin J. Klein's above-mentioned claim, according to which such a concept was only introduced in 1877, should be weakened at least. In fact, in the 1866-1871 theory of equilibrium remarkable anticipations of state probability can be found, which represents – at least implicitly – a third meaning of probability.

There are still two remarks I would like to make concerning Boltzmann's use of probabilistic arguments of the period 1866-1871. In the first place, Boltzmann's justification for using probabilistic concepts and arguments is radically different from Maxwell's. Boltzmann's first research programme dealt with the problem of cancelling out the details of motion. The echoes of this problem can be easily heard in the articles on kinetic theory, when he stated that the thermodynamic evolution of a system does not depend on the configurations of its molecules but on general parameters only.[72] As a consequence, while from Maxwell's point of view the use of the probability was justified by the human impossibility to have access to certain information, from Boltzmann's it was justified by the fact that such information is *irrelevant*: we really don't need to know the exact trajectory of the system, but we can limit ourselves to consider the general constraints (energy and momenta conservation) and to perform a combinatorial analysis of the resulting phase space suitably divided into elementary events.

In the second place, Boltzmann claimed that probabilistic arguments are not less reliable than dynamical arguments usually applied in mechanics. Boltzmann's point is that conclusions follow from probabilistic arguments in a way that is no less exact and no less logically consistent than the conclusions reached with other kind of arguments. What is different is only the set of presuppositions. If these presuppositions are satisfied (which always happens in structures as complex as gases), the conclusions follow with equal certainty. In other words, the connection between presuppositions and conclusions is a logical one and it is not a matter of (higher or lower) probability.[73]

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[72] Cf. e.g., Boltzmann 1871b, 240, 255.
[73] Cf. Boltzmann 1871b, 255; 1872, 317-318.

5. *THE TRANSITION TO THE NON EQUILIBRIUM THEORY.*

Boltzmann's special theoretical background in developing the equilibrium theory made possible the non equilibrium theory in 1872. Boltzmann's research programme did not focus on a single state of the system, as Maxwell's did, but on its whole evolution, and this implied a radical alteration of the view of equilibrium. According to Maxwell, equilibrium is characterized by mechanical and thermal neutrality (mutual balance of the collisions and equilibrium of temperature). On the contrary, Boltzmann mainly understands equilibrium *as the final point of a process* that can be described by the change of the distribution function:[74]

> As the time goes, the state of each molecule will constantly change by means of the motion of its atoms during the rectilinear motion, as well as by means of its collisions with other molecules; thus, generally speaking, the form of the function *f* will change, until this function will assume a value that will not be changed further by the motion of the atoms and by the collisions of the molecules. If this happens, we will say that, the molecules find themselves […] in *equilibrium*.

This meaning of equilibrium stems directly from the connection between the irreversible thermodynamics processes and the variational principles. In this sense, as I mentioned above, Boltzmann's important result in 1866 was the discovery that the principle of least action is the mechanical analogy of the Second Law.

Boltzmann's non equilibrium theory was first presented in 1872 in the long paper "Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen" whose main structure he had been preparing during his period in Berlin.[75] In this theory, many ideas put forward in the equilibrium theory of 1866-1871 come together. For instance, in the introduction to his article, Boltzmann exposed both his general position about statistical arguments, and the dualism between simultaneous and temporal diffusion.[76] But still more remarkable is the fact that the equilibrium theory prepared the theory of 1872 from a formal point of view as well. It seems to me that historians have not paid sufficient attention to this point, in particular to the contribution of the equilibrium theory to the construction of the famous Boltzmann equation. In order to obtain his equation, Boltzmann needed two fundamental ingredients: a suitable collision mechanism and the direct comparison of states with different dynamical histories.

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[74] Boltzmann 1871b, 240.

[75] In a famous letter to his mother on 27 January 1872, Boltzmann writes about having given a summary of the paper before the Berliner Physikalischen Gesellschaft. However, the talk attracted no attemption, except for some remarks of Helmholtz (cf. Höflechner 1994, II 9).

[76] Cf. Boltzmann 1872, 317, where he stated that an 'exact theory' of gases requires the calculation of 'the probability of the different states following one another in a large interval of time for a single molecule and [of different states] of many molecules simultaneously.'

The first ingredient is due to the fact that the reversible collision mechanism used in the previous papers was not able to bring a system into equilibrium starting from an arbitrary state. In order to introduce an 'exact consideration of the collision process,'[77] Boltzmann discusses the temporal variation of the distribution function as the result of a balance between entering and exiting molecules in and from any energy region.[78] A generic collision concerns particles whose kinetic energy changes from the entering pair ($\mathbf{x}$, $\mathbf{x}'$) to the exiting pair ($\mathbf{y}$, $\mathbf{y}'$). In other words, the particles have kinetic energy $\mathbf{x}$ and $\mathbf{x}'$ before the collision, $\mathbf{y}$ and $\mathbf{y}'$ after the collision. The number of collisions causing the exit of a molecule from the energy region $\mathbf{x}$ during the infinitesimal time interval τ is:[79]

$$\int dn = \tau f(\mathbf{x},t)d\mathbf{x}\int_0^\infty \int_0^{x+x'} f(\mathbf{x}',t)\psi d\mathbf{x}'d\mathbf{y}, \tag{16}$$

where ψ is a function collecting all the collision parameters (e.g. scattering angles, directions of motion and so on). The equation (16) has two characteristics that make Boltzmann's collision mechanism absolutely original.

In the first place, note the limits of the integrations. The entering kinetic energy $\mathbf{x}'$ can assume every possible value from 0 to ∞ meaning that a particle can collide with particles whatever their energy. This statement rests on the variety of motion conditions: indeed Boltzmann explicitly assumes that all the possible positions and directions of motion are *equiprobable*.[80] Furthermore, once the entering energies are fixed, a constraint for the total energy of the collision process is given, then the exiting energies have to find themselved included within the interval $\mathbf{x} + \mathbf{x}'$. Hence, only one exiting energy has to be determined, because the other one is automatically provided by the total energy constraint. But the important step in the equation (16) is that the exiting energy $\mathbf{y}$ is integrated *for all the possible values* from 0 to $\mathbf{x} + \mathbf{x}'$. This means that in Boltzmann's collision mechanism an arbitrary pair of entering energies ($\mathbf{x}$, $\mathbf{x}'$) *can originate any exiting energy between 0 and* $\boldsymbol{x} + \boldsymbol{x}'$.

In the second place, it is worth noting the use of the distribution function. The probability of a collision with entering energy $\mathbf{x}'$ directly depends on the value of the distribution function for that energy. This assumption was already put forward by Maxwell and amounts to say that the probability of a collision with a molecule with a certain velocity depends only on the number of molecules having

[77] Boltzmann 1872, 324.
[78] In 1872 Boltzmann used a distribution function depending on energies only. This fact caused him several problems in the combinatorial derivation of the Maxwell distribution in three dimensions. To avoid these problems, in the great memoir of 1877 Boltzmann dealt with a function of the three components of velocity.
[79] Boltzmann 1872, 342. Note that Boltzmann, in *Analytischer Beweis*, 289-293 proposed a very similar analysis of collision. The difference was that he evaluated the balance for only one elementary region, rather than to discuss the collision as a complex process.
[80] Boltzmann 1872, 321-322.

that velocity.[81] However, in the equation (16) no particular distribution function is framed for **y**. Hence in the selection of the exiting energies, all the ordinate pairs (**y**, **y**′) *are considered equiprobable*, that is, for such pairs a uniform distribution is supposed.

The deep difference between this way of understanding the role of collision and Maxwell's (or even Boltzmann's in 1868) is transparent. There are no longer intricated mechanical and geometrical investigation on the relations among scattering angles, directions of motion, velocities, and so on. On the contrary, Boltzmann simply *supposes* that the equiprobability of the collision parameters allows the collisions to occur in a way able to guarantee the equiprobability of the exiting energies. Thus, the dynamical links existing between the two pairs of energies have been dissolved, because the definition of the entering energies and the definition of the exiting energies have become two *independent* processes. Indeed, Boltzmann's collision mechanism can be probabilistically understood as a two-step process of drawing. At the first step, the entering energies are drawn from their real distribution in the system, but, at the second step, the exiting pairs of energies are drawn from a uniform distribution constrained by the principle of conservation of energy only. This feature allows the mechanism to change the distribution on the system: the entering molecules are selected according to the starting distribution, but the exiting molecules are selected in a distribution *which is uniform on the elementary regions d***y**. Of course, in the long run this process succeeds to transform the starting distribution into Maxwell's distribution. From this point of view, no wonder that Boltzmann's theory leads to the equilibrium state, as further proved by the *H*-theorem. In fact, the collision mechanism is framed in order to obtain such a result. Similar remarks hold for the number of collisions increasing the molecules contained in the energy region **x**.

The structure of Boltzmann's collision mechanism of 1872 is less surprising when his previous results in equilibrium theory are taken into account. Indeed, it is framed in order to obtain a uniform distribution on the elementary events, the condition of equilibrium Boltzmann was aware of since 1868, and which he had called the General Solution: the close connection between equilibrium and equiprobability, contained in the Boltzmann-Liouville theorem, is the foundation of the new non equilibrium theory. Thus, in non equilibrium theory Boltzmann focusses less and less on the purely mechanical aspects of the collisions, but more and more on their stocastic and probabilistic elements.

The second ingredient needed for the Boltzmann equation, namely the possibility of compare two states with different dynamical histories, becomes

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[81] This assumption is known as *Stosszahlansatz*, (assumption on the number of collisions) cf. Ehrenfest 1911, 10-13.

essential when Boltzmann finally obtains a unique differential equation for the distribution function:[82]

(17)
$$\frac{\partial f}{\partial t} = \int_0^{\infty} \int_0^{x+x'} \left[f(\mathbf{y},t) f(\mathbf{x}+\mathbf{x}'-\mathbf{y},t)\psi' - f(\mathbf{x},t) f(\mathbf{x}',t)\psi \right] d\mathbf{x}' d\mathbf{y}.$$

In the equation (17) a direct comparison between the different values of the distribution function is possible only knowing the function ψ expressing the dynamical detail of the collision process. Hence, in order to use the equation (17) to get information about the evolution of the system, we would have to know the exact sequence of the value of the ψ function, i.e. the sequence of collisions that the particle undergoes. The value of the ψ function are the details of particles motion. But Boltzmann claims that the function ψ remains constant, i.e. in all the phase space the equality $\psi = \psi'$ holds.[83] This result is not proved in the paper, but he refers to his previous work about the connection between the Boltzmann-Liouville theorem and the Jacobi's principle of the last multplier. From this, with some suitable simplifications, Boltzmann's equation in its usual form immediately follows:

(18)
$$\frac{\partial f}{\partial t} = \int_0^{\infty} \int_0^{x+x'} \left[f(\mathbf{y},t) f(\mathbf{x}+\mathbf{x}'-\mathbf{y},t) - f(\mathbf{x},t) f(\mathbf{x}',t) \right] \psi d\mathbf{x}' d\mathbf{y}.$$

Thus, once more the diffusion, in the form of the Boltzmann-Liouville theorem, holds the spotlight. To get the equation (18), the famous Boltzmann equation, from the equation (17) it is necessary to neclect the details of motion depending on the sequence of collision i.e. to make the evolution of the system depending on the distribution function only. But, the various elements necessary to Boltzmann's theory are connected by mutually logical relationships that are far from clear and the final result is not completely consistent. Elements coming from mechanics and elements coming from the combinatorial analysis are mixed to a level even deeper than in 1868. The first birth-cries of a new physical concept, that of the statistical-mechanical system, present us with an inconsistent entity where different factors from mechanics, formal theory of probability and Boltzmann's particular interpretation of statistical arguments come together.

6. *BOLTZMANN'S THEORY IN RETROSPECT.*

In the previous sections I have argued that for understanding Boltzmann's approach to thermodynamics the 1866 paper on the mechanical analogy of the second principle plays a crucial role. In that article, we can find, in hindsight, the root of the most fundamental concepts of Boltzmann's theory, in particular the

[82] Boltzmann 1872, 332.
[83] Boltzmann 1872, 332-334.

ergodic hypothesis. But this does not mean that these concepts stemmed from the root automatically. As we have seen, Boltzmann looked at the use of the principle of least action in 1866 as a way to extend the ambit of analitical mechanics to include thermodynamical systems. In Boltzmann's hands, the tools of mechanics show a flexibility and a pliability that they had not in Clausius'. In particular, the concept of diffuse motion represents a significant step towards a fruitful application of analytical mechanics to the dynamical theory of heat.

But this flexible use of the mechanical tools and this stretching of the limits of classical mechanics itself had a price: in its attempt to explore a new territory, Boltzmann's thought is crossed by internal conceptual tensions which are very apparent in his papers. The works of the Austrian physicist are known to be extremely lenghty and full of intricate calculations which sometimes give the impression of concealing some conceptual gaps. His arguments often are unclear and, above all, some fundamental steps are scantly justified. A good example is the combinatorial analysis in 1868, a piece of high statistics decades ahead of its time, which is introduced with no foundation at all after thirty pages of standard mechanical calculation on the collision process. Another sign of the internal conceptual tensions in Boltzmann's thought is his continous re-analyzing the problem from many different points of view. In the 1871 trilogy, Boltzmann's concern to relate the concept of diffusion to other firm principles of analytical mechanics, in particular Jacobi's principle of the last multiplier, clearly emerges. His mechanical model of diffuse motion points in the same direction: making this concept more acceptable and understandable. Moreover, and this is a further hint of the above mentioned tensions, Boltzmann never states the ergodic hypothesis as openly as Maxwell. He makes plenty of attempts to shed light upon its conceptual core, but he did not understand it simply as an additional hypothesis to the mechanical analysis: Boltzmann's goal was to integrate this hypothesis in the mechanical conceptual framework.

Finally, characteristic of the tensions in Boltzmann's thought is also the oscillation between mechanical and statistical arguments. Since his paper on the equilibrium theory of 1868, he desperately tries to conciliate mechanical and stochastic processes, and the result of these efforts is a progressive depletion of the role of collisions. In the 1868 paper, the collision analysis occupies most of the paper and it is pursued in a completely standard way. But, as we have seen, in 1872 the mechanical features of the collisions become less relevant than the stochastic features. The collision mechanism proposed in 1872 is mainly a stochastic process with some mechanical elements. Eventually, in 1877 collisions play no longer a role: Boltzmann's theory becomes completely combinatorial, and the particular physical mechanism beneath the non equilibrium process is out of focus. In fact, the mechanical and geometrical analysis of the collisions is replaced by equiprobability assumptions about the collision parameters.

At the same time, the increasing importance of the combinatorial analysis is closely related to the particular issues faced by Boltzmann in 1866. The mechanical analogy of the Second Law is the principle of least action, i.e. a variational principle. It states that the real trajectory followed by the system is such that the action integral is a minimum *among all the possibile trajectories within the same general constraints*. Thus, the principle of least action requires a comparison between all the possible evolutions of the system and a proof that the real one is privileged with respect to the other. This is exactly the strategy that Boltzmann put forward in 1868 and 1877 by means of his combinatorial calculation of all the possible combinations of elementary events in the energy space. The combinatorial analysis allows to compare all the possible states by means of suitable statistical weights, and Boltzmann succeeds in proving that the increasing-entropy process is the one with the greatest statistical weight. Hence, a clear parallelism can be seen between the comparison of reality and virtuality implicit in the analytical mechanics and in the combinatorial approach to the thermodynamical problems.

7. *Concluding remarks.*

Throughout the period 1866-1871, Boltzmann investigated the problem of the equilibrium states and developed the statistical techniques and the assumptions founding them. These analyses led to the conceptual core of the new theory of non equilibrium: the collision mechanism and the Boltzmann equation. The results obtained in 1866-1871, which can be seen at work in the theory of 1872, are the Boltzmann-Liouville theorem, the diffusion of motion, the equiprobability of the elementary volumes. This implies a partial revision of some well-founded historical views concerning the conceptual development of Boltzmann's theory. In particular, I will mention two of them.

The first consequence is that Boltzmann's non equilibrium theory is not an isolated phenomenon, rather, it is closely connected to the equilibrium theory and to the research programme which generated it. It has to be contextualized in the broader framework of the analytical study of the free evolution of a system of material points. This is proved by the fact that many ideas constituting the core of the non equilibrium theory can be found in Szily's and Clausius' papers as well. Furthermore, Jan von Plato claimed that Boltzmann interpreted the ergodic motion of a system as a complex of periodical motions.[84] A very similar idea can be found as a consequence of Clausius' stationary motion. These ideas were, let's say, in the air, as the case of the nearly contemporaneous discovery of mechanical analogy teaches us. However, Boltzmann assimilated them differently from Clausius and Maxwell, developing a general analysis of the non equilibrium theory. On the contrary, Clausius and Maxwell dealt with the problem of non

[84] Von Plato 1991, 81.

equilibrium only from the point of view of the thermodynamics and the transport phenomena.

The second consequence is that the theory of 1872 is not a purely mechanical theory as was often claimed. This opinion is partially due to the frequent use made by Boltzmann of the expression 'analytical proof.'[85] However, according to his point of view, analytical proof means an argument in which the conclusions logically follow from the premises. Boltzmann was aware that his theory relied on probabilistic assumptions such as the diffusion of motion and that his results held on average only. Already in 1868, discussing the equilibrium theory, he explicitly stated that some exceptions existed due to the possibility that the assumption of mutual independence of the phase coordinates did not hold, 'e.g. if all the points and the fixed centre are set in a line of a plane.'[86] In this case, the motion would not be diffuse and an essential condition for the probabilistic argument would fail. Analogously, the *H*-theorem was proved by Boltzmann averaging among the possible evolutions of the *H*-function with regard to each parameter of collision.[87] Furthermore, both the collision mechanism and the Boltzmann equation relied on assumptions that were not entirely dynamical, as Maxwell pointed out in 1879 and as Boltzmann recognized from 1868 on.

[85] Klein 1973, 73.
[86] Boltzmann 1868, 96.
[87] Boltzmann 1872, 335-344.

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